



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 18/48	A1	(11) International Publication Number: WO 96/23827 (43) International Publication Date: 8 August 1996 (08.08.96)
(21) International Application Number: PCT/US96/01425 (22) International Filing Date: 2 February 1996 (02.02.96) (30) Priority Data: 08/382,562 2 February 1995 (02.02.95) US Not furnished 1 February 1996 (01.02.96) US (71) Applicant: SIMULA INC. [US/US]; 10016 S. 51st Street, Phoenix, AZ 85044 (US). (72) Inventor: SLAGEL, Edwin, C.; 10920 Sieno Place, Avondale, AZ 85323 (US). (74) Agents: GOTTS, Lawrence, J. et al.; Crowell & Moring, 1001 Pennsylvania Avenue, N.W., Washington, DC 20004-2595 (US).		(81) Designated States: CA, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: IMPACT RESISTANT POLYURETHANE AND METHOD OF MANUFACTURE THEREOF (57) Abstract The present invention is an optically clear impact resistant polyurethane which provides exceptionally high heat distortion temperatures and excellent chemical resistance. The invention is particularly useful for transparency applications that require excellent impact resistance coupled with high heat distortion temperatures, such as glazings for buildings, vehicles, riot shields, aircraft canopies, and face masks.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**IMPACT RESISTANT POLYURETHANE
AND METHOD OF MANUFACTURE THEREOF**

BACKGROUND

Field of the Invention

The present invention relates to optically transparent heat and impact resistant polyurethane.

Background of the Invention

Currently, the standard material to which all optically transparent plastic materials are compared to for impact resistance is polycarbonate. These materials can be characterized by the temperature and pressure at which the material undergoes distortion. The heat distortion temperature of 9034 series clear polycarbonate is 280°F at 264 psi.

Polycarbonate has a V-50 0.22 cal FSP (fragment simulating projectile) impacting rating of 925 ft./sec. This means that 50% of 22-caliber projectiles fired through a 0.250" polycarbonate sheet penetrate a 20 mils-thick 2024 T6 aluminum sheet (the "witness sheet") placed 6 inches behind the back surface of the poly carbonate sheet.

U.S. Patent No. 3,866,242, which is incorporated herein by reference, discloses a polyurethane polymer protective shield. The polyurethane is produced by:

(a) reacting either a polyether glycol or a polyester glycol having a molecular weight of about 700 to 1,000 with methylenebis(cyclohexyl isocyanate) in an equivalent ratio of about three NCO to each hydroxyl to form a prepolymer, and

(b) reacting the prepolymer with an aromatic amine curing agent having a methylene bridge between two aromatic rings, such as 4,4'-methylenebis(2-chloroaniline), in an equivalent ratio of 0.90 to 1.04 $\text{NH}_2/1.0$ NCO.

U.S. Patent No. 4,808,690, which is incorporated by reference herein, discloses a transparent polyurethane polymer made from a polyol cured prepolymer. The prepolymer is made from a polyisocyanate and at least one multifunctional hydroxy-containing intermediate.

SUMMARY OF THE INVENTION

The optically clear polyurethane of this invention can be prepared by first producing a prepolymer by reacting one equivalent of a polyester glycol or a polyether glycol having a weight average molecular weight of between about 600 and about 1200 with 4,4'-methylenebis(cyclohexyl isocyanate) in an equivalent ratio of 2.5 to 4.5 NCO for each OH, with a preferable ratio of about 3 to 3.5 NCO for each OH. The prepolymer is then reacted with an aromatic diamine curing agent such as 4,4'-methylenebis(3-chloro-2,6-diethylaniline) in an equivalent ratio of 0.95 to 1.02 $\text{NH}_2/1.0$ NCO, with the preferred range being 0.96 to 1.0 $\text{NH}_2/1.0$ NCO.

The polyurethane of the present invention is particularly useful for transparency applications that require excellent impact resistance coupled with high heat distortion temperatures, such as glazings for buildings, vehicles, riot shields, aircraft canopies and face masks.

One object of this invention is to provide a method for producing optically transparent plastic sheets for use in applications requiring excellent impact resistance, excellent chemical resistance, and high heat distortion temperatures.

Another object of this invention is to provide transparent polyurethanes having excellent optical clarity, excellent ballistic properties, and high heat distortion temperatures compared to prior art materials.

These and other objects of the present invention are described in greater detail in the detailed description of the invention, the examples and the attached claims.

DETAILED DESCRIPTION OF THE INVENTION

The polyurethane of the present invention is prepared from aliphatic diisocyanates; OH-containing intermediates selected from polyester glycols, polyether glycols and mixtures thereof; and aromatic diamine curing agents. The following is a detailed description of each of these constituents:

OH-Containing Intermediates

The OH-containing intermediates which can be used to prepare the polyurethanes of this invention are polyether glycols and polyester glycols having a weight average molecular weight of between about 500 to about 1,200. Polyether glycols and polyester glycols having molecular weights of about 600 to 900 are especially effective. Polyether glycols that can be used include polytetramethylene ether glycols having a weight average molecular weight of between about 500 and about 1000.

Representative polyesters which can be used to prepare the compositions of this invention include polycaprolactones and polyesters based on esterification of dicarboxylic acids of four to ten carbon atoms, such as adipic, succinic and sebacic acids, in the presence of low molecular weight glycols of two to ten carbon atoms, such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, 1,6-hexanediol and 1,10-decanediol. The polycaprolactones are prepared by condensing caprolactone in the presence of difunctional active hydrogen compounds such as water or the low molecular weight glycols listed above. Polyesters obtained by esterification of caprolactones, dicarboxylic acids and glycols can be derived by well known esterification or transesterification procedures, as described, for example, in the article D.M. Young, F. Hostettler et al., "Polyesters from Lactone," Union Carbide F-40, p. 147. The preferred OH-containing intermediates are polyester glycols that are the esterification products of adipic acid or caprolactone with glycols of two to ten carbon atoms. The most preferred OH-containing intermediates are 1,6-hexanediol adipate, or 1,10-decanediol adipate, and 1,10-decanediol caprolactone.

Isocyanates

The isocyanates which can be used to prepare the polyurethanes of this invention include diisocyanato-dicyclohexylmethanes and preferably isomeric mixtures thereof containing from about 20-100 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate), hereinafter referred to as "PICM." Other components usually present in the mixtures of

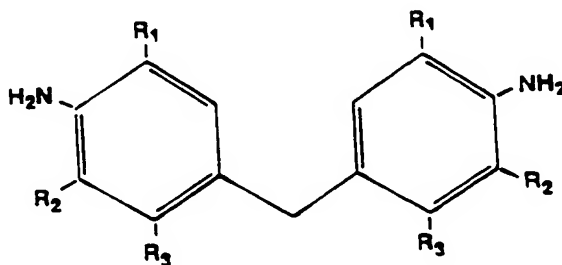
position and/or stereoisomers of the diisocyanato-dicyclohexylmethane used in this invention are the cis.trans and cis.cis isomers of PICM and stereoisomers of 2,4'-methylenebis(cyclohexyl isocyanate). These, as well as the trans.trans PICM isomer, are present in amounts which can be controlled by the procedures used to prepare the diisocyanato-dicyclohexylmethane. Preferred diisocyanates are isomeric PICM mixtures. An especially preferred mixture contains not less than about 50 percent of the trans.trans trans isomer and no more than about 20 percent of the cis.cis isomer of 4,4'-methylenebis(cyclohexyl isocyanate). This preferred mixture, when reacted with a polyester glycol and cured with 4,4'-methylenebis(3-chloro-2,6-diethylaniline) produces a high-quality impact-resistant, transparent polyurethane.

The PICM used in this invention is prepared by phosgenating the corresponding 4,4'-methylenebis(cyclohexyl amine) (PACM) by procedures well known in the art, as disclosed in, *e.g.*, U.S. Patent Nos. 2,644,007, 2,680,127, and 2,908,703, which are incorporated herein by reference. The PACM isomer mixtures, upon phosgenation, yield PICM in a liquid phase, a partially liquid phase, or a solid phase at room temperature. The PACM isomer mixtures can be obtained by the hydrogenation of methylenedianiline and/or by fractional crystallization of PACM isomer mixtures in the presence of water and alcohols such as methanol and ethanol.

Diamine Curing Agents

The aromatic diamine curing agents which can be used in the preparation of the polyurethanes of this invention have only primary amine

groups. The preferred diamine curing agents have the following chemical formula:



wherein R_1 and R_2 are each independently selected from methyl, ethyl, propyl, and isopropyl groups, and R_3 is selected from hydrogen and chlorine. Examples of the preferred diamine curing agents are the following compounds, manufactured by Lonza Ltd. (Basel, Switzerland):

LONZACURE® M-DIPA	$R_1 = C_3H_7; R_2 = C_3H_7; R_3 = H$
LONZACURE® M-DMA:	$R_1 = CH_3; R_2 = CH_3; R_3 = H$
LONZACURE® M-MEA:	$R_1 = CH_3; R_2 = C_2H_5; R_3 = H$
LONZACURE® M-DEA:	$R_1 = C_2H_5; R_2 = C_2H_5; R_3 = H$
LONZACURE® M-MIPA:	$R_1 = CH_3; R_2 = C_3H_7; R_3 = H$
LONZACURE® M-CDEA:	$R_1 = C_2H_5; R_2 = C_2H_5; R_3 = Cl$

wherein R_1 , R_2 and R_3 refer to the above chemical formula. Lonzacure® M-CDEA is available in the United States from Air Products and Chemical, Inc. (Allentown, Pennsylvania). The preferred diamine curing agent is 4,4'-methylenabis(3-chloro-2,6-diethylaniline).

Preparation of the Invention

The polyurethanes of this invention can be prepared by one shot, quasi-prepolymer or full prepolymer methods, all of which are well known in the art. The preferred method of preparing the polyurethanes according to the invention is as follows: The methylenebis(cyclohexyl isocyanate) is first mixed with the OH-containing intermediate in an equivalent ratio of 2.5 to 4.5 NCO/1.0 OH and then heated to 190-275°F, preferably 260-275°F. The mixture is then heated under dry nitrogen so that the methylenebis(cyclohexyl isocyanate) reacts with the OH-containing intermediate to form a prepolymer. The heat source is then removed, the prepolymer is cooled to about 160°F, and the percent NCO in the prepolymer is determined. Additional methylenebis(cyclohexyl isocyanate) is then added to achieve an equivalent weight of from 415 to 425. The prepolymer is then reacted with the aromatic diamine curing agent in an equivalent ratio of 0.95 to 1.02 NH_2 /1.0 NCO. The prepolymer is then cured at 240-275°F for 4 to 16 hours. The curing time is longer for the lower temperatures and shorter for the higher temperatures.

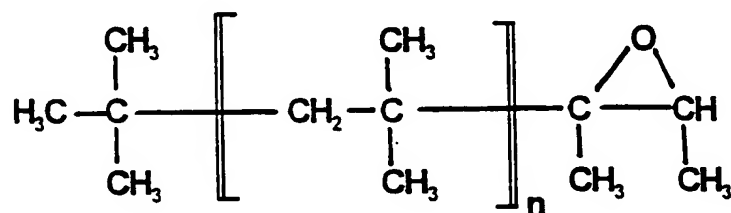
Preferred prepolymers for use in the present invention are prepared from adipic acid/hexanediol polyester having a weight average molecular weight of about 1000 and 4-4'-methylenebis(cyclohexyl isocyanate) containing a minimum of 50% of the trans,trans isomer, and a maximum of 20% cis,cis isomer PICM. The equivalent ratio of NCO groups to OH groups is about three to one.

The polyurethane polymers of this invention can be cast, compression molded, extruded or injection molded. Casting is the preferred method, because it produces a polyurethane polymer with optimal optical characteristics.

The prepolymer may be cast in a mold prior to curing. The polyurethane material according to the invention may also be partially cured, by selecting an appropriate curing time and temperature, and then formed into the desired shape. Using this process, the polyurethane material can be formed into a simple or complex shape and then subsequently fully cured.

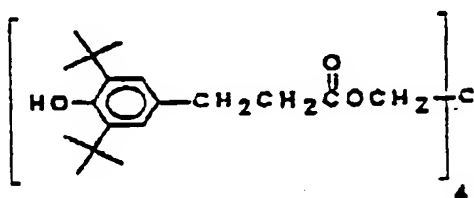
A triol may be added to the prepolymer in an amount sufficient to produce one percent cross-linking based upon equivalents of reactants, for example 4 to 8% by weight based on total reactants. Triols that are useful in the present invention include trimethylol ethane and trimethylol propane. The addition of a triol to the prepolymer increases the heat distortion temperature and improves the ballistics properties of the cured polyurethane.

The impact and crack propagation resistance of the polyurethanes according to the invention may be improved by the addition of an activated polybutene with epoxide functionality at one end in order to promote the formation of micro voids in the polyurethane. An activated polybutene may be added to the prepolymer in an amount ranging from 2.0 to 2.5% by weight based on the prepolymer without adversely affecting the desired optical and heat distortion properties. The addition of amounts greater than 2.5% by weight may result in a translucent or opaque polyurethane. Activated polybutenes that are useful in the present invention include compounds of the following formula:



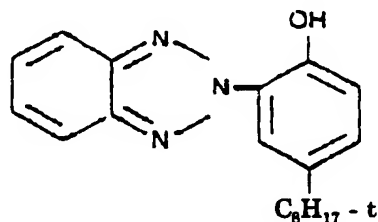
where n has a range of values such that the weight average molecular weight is about 365. One example of such an activated polybutene is Actipol E6, available from Elf Atochem.

Various anti-oxidants, ultraviolet stabilizers, and mold release agents may be used in the preparation of the polyurethanes of this invention. For example, one or more anti-oxidants may be added to the prepolymer in an amount of from 1 to 5% by weight based on total reactants. Anti-oxidants that are useful in the present invention include those of the multifunctional hindered phenol type. One example of a multifunctional hindered phenol type anti-oxidant is Irganox 1010, available from Ciba Geigy, which has the following chemical formula:

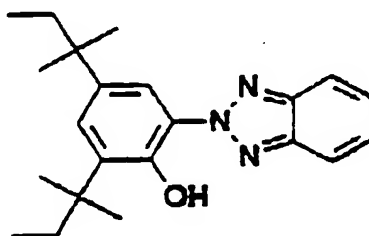


A UV-stabilizer may also be added to the prepolymer, either prior to or during the curing step, in an amount of from 1.5 to 2.0% by weight based on total reactants. UV-stabilizers that are useful in the present invention include

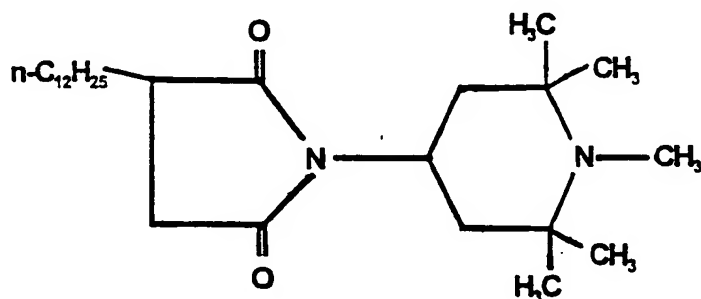
benzotriazoles. Examples of benzotriazole UV-stabilizers include Cyasorb 5411 and Tinuvin 328. Cyasorb 5411, available from American Cyanamid, has the following chemical formula:



Tinuvin 328, available from Ciba Geigy, has the following chemical formula:



Another UV-stabilizer that may be used is Cyasorb 3604, available from American Cyanamid, which has the following chemical formula:



The polyurethanes of the present invention may be cast between glass plates, and the glass plates may be advantageously coated with a mold release agent prior to casting. Mold release agents that are useful in the present invention include silanes, for example Repcon rain repellent, available from Unelko Corporation (Chicago, Illinois).

EXAMPLES

In the following examples, all parts are by equivalent weight or weight percent unless otherwise indicated. These examples are illustrative and representative of the various embodiments of the present invention described above.

The materials used in the following examples were obtained from the following commercial sources:

4,4'-methylenebis(cyclohexyl isocyanate)	Miles Industrial Chemicals
1,6-hexanediol adipate	RUCO Polymer Corporation
4,4'-methylenebis(3-chloro-2,6-diethylaniline)	Air Products and Chemicals, Inc.
trimethylol propane	Hoechst Celanese
trimethylol ethane	Aldrich
Irganox 1010	Ciba Geigy
Cyasorb 5411	American Cyanamid
Cyasorb 3604	American Cyanamid
Tinuvin 328	Ciba Geigy
Actipol E6	Elf Atochem

Repcon

Unelko Corporation

Example I

A polymer was prepared by adding 2.187 parts of 1,6-hexanediol adipate (molecular weight 1,038) to 1.813 parts of 4,4'-methylenebis(cyclohexyl isocyanate) (containing approximately 50% of the trans,trans isomer) at 180-200°F. The mixture was agitated under a dry N₂ blanket and heated to a temperature of 275°F over a period of approximately 60 minutes, at which time the heat source was removed. The prepolymer was cooled to 160°F over approximately 30 minutes, and the percent NCO was determined. (The cool down time period is not a critical parameter.) Additional 4,4'-methylenebis(cyclohexyl isocyanate) was added to achieve an equivalent weight of 420. The prepolymer was then reacted with 4,4'-methylenebis(3-chloro-2,6-diethylaniline) in an equivalent ratio of 1.0 NCO to 0.98 NH₂ groups. The polymer was cast between glass plates so as to produce an optical sheet 0.25 inches x 12 inches x 12 inches, and was then cured at 250°F for 12 hours. The glass plates were coated with Repcon rain repellent as a mold release.

The cured polyurethane sheet exhibited the following properties:

Luminous transmittance	85%
Haze	3.5%
Hardness Shore "D"	80-81
Heat Distortion at 264 psi	302°F
V-50, 0.22 cal FSP	1180 ft./sec.

The luminous transmittance and haze were measured using a Gardner Laboratory XL 230 colorimeter.

Example II

To the prepolymer prepared according to Example I. 1.5% Cyasorb 5411 and 0.2% Irganox 1010 were added. based upon the prepolymer weight. Prior to casting the prepolymer, 0.25% Cyasorb 3604 was added based upon the total weight of the reactants (including the weight of the curing agent). The mixture was then cast and cured as described in Example I. The cured polyurethane sheet exhibited the following properties:

Luminous transmittance	85%
Haze	3.5%
Hardness Shore "D"	80-81
V-50 0.22 cal FSP	1192 ft./sec.
1000 hour accelerated ultraviolet exposure	No change in the above properties
2000 hour accelerated ultraviolet exposure	No change in the above properties
6 month outdoor weathering (Phoenix. AZ)	Virtually no change in the above properties

The luminous transmittance and the haze were measured as in Example I. The ballistic properties of the polyurethane material were not affected by either the accelerated ultraviolet exposure or the outdoor weathering.

Example III

To the prepolymer prepared according to Example II, trimethylol propane ("TMP") was added so as to produce one percent cross-linking based upon equivalents of reactants. A 0.25 x 12 x 12 inch test sheet was cast, as in Example

I. The cured polyurethane sheet exhibited the following properties:

Luminous transmittance	85%
Haze	3.5%
Hardness Shore "D"	80-81
Heat distortion at 264 psi	320°F
V-50 0.22 cal FSP	1224 ft./sec.
Craze resistance to isopropyl alcohol	> 7,000

The luminous transmittance and the haze were measured as in Example I. The addition of TMP to the prepolymer improved both the heat distortion temperature and V-50 test as compared with Examples I and II. The V-50 test result shows a 34% improvement over polycarbonate, and the heat distortion temperature is 45°F higher than the heat distortion temperature of polycarbonate.

Example IV

To the prepolymer prepared according to Example II, 2.0 to 2.5 percent by weight Actipol E6 was added. The addition of the Actipol E6 further improved the impact and crack propagation resistance of the cured polyurethane sheet.

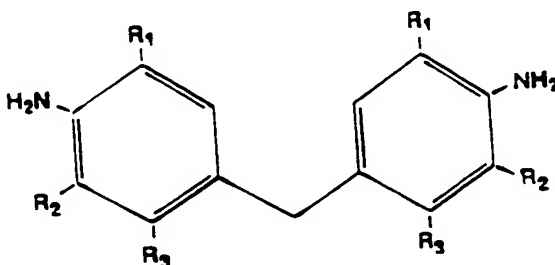
The foregoing disclosure of examples and other embodiments of the present invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise examples and embodiments disclosed. Many variations and modifications of the examples and embodiments described herein will be obvious to one of ordinary skill in the art in light of the above disclosure. The scope of the invention is to be defined only by the claims appended hereto, and by their equivalents.

WHAT IS CLAIMED IS:

1. A polyurethane material comprising the reaction product of:

(a) a polyurethane prepolymer prepared by reaction of methylenebis(cyclohexyl isocyanate) with an OH-containing intermediate having a weight average molecular weight between about 500 and about 1,200 selected from the group consisting of polyester glycols, polyether glycols, and mixtures thereof in an equivalent ratio of 2.5 to 4.5 NCO/1.0 OH; and

(b) an aromatic diamine curing agent having the formula:



wherein R₁ and R₂ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl groups, and R₃ is selected from the group consisting of hydrogen and chlorine, in an equivalent ratio of 0.95 to 1.02 NH₂/1.0 NCO.

2. The polyurethane material of claim 1, wherein R₃ is chlorine.

3. The polyurethane material of claim 1, wherein the diamine curing agent is 4,4'-methylenebis(3-chloro-2,6-diethylaniline).

4. The polyurethane material of claim 1, wherein the polyurethane material has a heat distortion temperature in the range of 210°F to 325°F at 264 psi.

5. The polyurethane material of claim 1. wherein the polyurethane material has a heat distortion temperature of at least 300°F at 264 psi.

6. The polyurethane material of claim 1. wherein the polyurethane material has a heat distortion temperature of at least 320°F at 264 psi.

7. The polyurethane material of claim 1, wherein the polyurethane material is optically clear having a luminous transmittance of at least about 85%.

8. The polyurethane material of claim 1. wherein a 0.25-inch thick sheet of the polyurethane material has a V-50 0.22 cal FSP rating of 1,100 to 1,400 feet/second.

9. The polyurethane material of claim 1, wherein the methylenebis(cyclohexyl isocyanate) is reacted with the OH-containing intermediate in an equivalent ratio of 3 to 3.5 NCO/1.0 OH.

10. The polyurethane material of claim 1, wherein the diamine curing agent is reacted with the prepolymer in an equivalent ratio of 0.96 to 1.0 NH_2 /1.0 NCO.

11. The polyurethane material of claim 1. wherein the weight average molecular weight of the OH-containing intermediate is between about 600 and about 900.

12. The polyurethane material of claim 1. wherein the OH-containing intermediate comprises at least one polyester glycol.

13. The polyurethane material of claim 12, wherein the polyester glycol is selected from the group consisting of 1,6-hexanediol adipate, 1,10-decanediol adipate, 1,10-decanediol caprolactone, and mixtures thereof.

14. The polyurethane material of claim 1, wherein the methylenebis(cyclohexyl isocyanate) comprises 20 to 100 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate).

15. The polyurethane material of claim 1, wherein the methylenebis(cyclohexyl isocyanate) comprises at least 50 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate).

16. The polyurethane material of claim 1, wherein the prepolymer further comprises an activated polybutene with an epoxide functionality on one end.

17. The polyurethane material of claim 16, wherein the activated polybutene is Actipol E6.

18. The polyurethane material of claim 1, wherein the prepolymer further comprises a UV-stabilizer.

19. The polyurethane material claim 18, wherein the UV-stabilizer is selected from the group consisting of Cyasorb and Tinuvin.

20. The polyurethane material of claim 1, wherein the prepolymer further comprises an anti-oxidant.

21. The polyurethane material of claim 19, wherein the anti-oxidant is Irganox.

22. The polyurethane material of claim 1, wherein the polyurethane material has excellent outdoor weathering characteristics.

23. The polyurethane material of claim 1, wherein the polyurethane material has excellent solvent resistance.

24. The polyurethane material of claim 1, wherein the prepolymer further comprises a triol in an amount sufficient to produce 1% cross-linking based upon equivalents of reactants.

25. The polyurethane material of claim 24, wherein the triol is selected from the group consisting of trimethylol ethane, trimethylol propane, and mixtures thereof.

26. A polyurethane material comprising the reaction product of:

(a) a polyurethane prepolymer prepared by reaction of 4,4'-methylenebis(cyclohexyl isocyanate) with a polyester glycol having a weight average molecular weight between about 600 and about 900 selected from the group consisting of 1,6-hexanediol adipate, 1,10-decanediol adipate, and mixtures thereof in an equivalent ratio of 2.5 to 4.5 NCO/1.0 OH; and

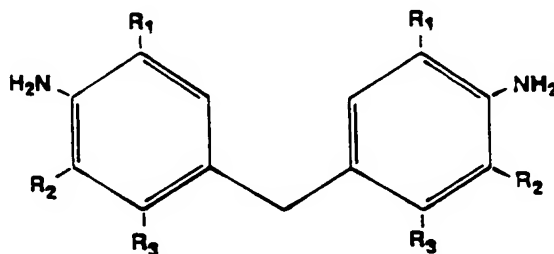
(b) 4,4'-methylenebis(3-chloro-2,6-diethylaniline) as a curing agent in an equivalent ratio of 0.95 to 1.02 NH_2 /1.0 NCO.

wherein the polyurethane material has a heat distortion temperature of at least 300°F at 264 psi.

27. A method for preparing polyurethane comprising the steps of:

(a) reacting methylenebis(cyclohexyl isocyanate) with an OH-containing intermediate having a weight average molecular weight between about 500 and about 1,200 selected from the group consisting of polyester glycols, polyether glycols, and mixtures thereof in an equivalent ratio of 2.5 to 4.5 NCO/1.0 OH to form a prepolymer; and

(b) reacting the prepolymer with an aromatic diamine curing agent having the formula:



wherein R₁ and R₂ are each independently selected from the group consisting of methyl, ethyl, propyl and isopropyl groups, and R₃ is selected from the group consisting of hydrogen and chlorine, in an equivalent ratio of 0.95 to 1.02 NH₂/1.0 NCO.

28. The method of claim 27, wherein R₃ is chlorine.

29. The method of claim 27, wherein the diamine curing agent is 4,4'-methylenebis(3-chloro-2,6-diethylaniline).

30. The method of claim 27, wherein the methylenebis(cyclohexyl isocyanate) is reacted with the OH-containing intermediate in an equivalent ratio of 3 to 3.5 NCO/1.0 OH.

31. The method of claim 27, wherein the diamine curing agent is reacted with the prepolymer in an equivalent ratio of 0.96 to 1.0 NH_2 /1.0 NCO.
32. The method of claim 27, wherein the weight average molecular weight of the OH-containing intermediate is between about 600 and about 900.
33. The method of claim 27, wherein the OH-containing intermediate comprises at least one polyester glycol.
34. The method of claim 33, wherein the polyester glycol is selected from the group consisting of 1,6-hexanediol adipate, 1,10-decanediol adipate, 1,10-decanediol caprolactone, and mixtures thereof.
35. The method of claim 27, wherein the methylenebis(cyclohexyl isocyanate) comprises 20 to 100 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate).
36. The method of claim 27, wherein the methylenebis(cyclohexyl isocyanate) comprises at least 50 percent of the trans,trans isomer of 4,4'-methylenebis(cyclohexyl isocyanate).
37. The method of claim 27, wherein an activated polybutene polymer with an epoxide functionality on one end is added to the prepolymer.
38. The method of claim 27, wherein a UV-stabilizer is added to the prepolymer.
39. The method of claim 38, wherein the UV-stabilizer is selected from the group consisting of Cyabsorb and Tinuvin.
40. The method of claim 27, wherein an anti-oxidant is added to the prepolymer.

41. The method of claim 40, wherein the anti-oxidant is Irganox.
42. The method of claim 27, further comprising adding a quantity of triol sufficient to produce 1% cross-linking based upon equivalents of reactants.
43. The method of claim 42, wherein the triol is selected from the group consisting of trimethylol ethane, trimethylol propane, and mixtures thereof.
44. A method for preparing polyurethane comprising the steps of:
 - (a) reacting 4,4'-methylenebis(cyclohexyl isocyanate) with a polyester glycol having a weight average molecular weight between about 600 and about 900 selected from the group consisting of 1,6-hexanediol adipate, 1,10-decanediol adipate, 1,10-decanediol caprolactone, and mixtures thereof in an equivalent ratio of 2.5 to 4.5 NCO/1.0 OH; and
 - (b) reacting the prepolymer with 4,4'-methylenebis(3-chloro-2,6-diethylaniline) as a curing agent in an equivalent ratio of 0.95 to 1.02 NH_2 /1.0 NCO.
45. A method for preparing polyurethane comprising the steps of:
 - (a) mixing 4,4'-methylenebis(cyclohexyl isocyanate) with an OH-containing intermediate having a weight average molecular weight of between about 500 and about 1,200 selected from the group consisting of polyester glycols, polyether glycols, and mixtures thereof in an equivalent ratio of 2.5 to 4.5 NCO/1.0 OH at about 180-200°F to produce a mixture;
 - (b) heating the mixture with a heat source under dry nitrogen to about 190-275°F so that said 4,4'-methylenebis(cyclohexyl isocyanate) reacts with said OH-containing intermediate to produce a prepolymer;

(c) removing the heat source and cooling the prepolymer to below 160°F;

(d) determining the percent of NCO in the prepolymer:

(e) adding 4,4'-methylenebis(cyclohexyl isocyanate) to the prepolymer so that the equivalent weight of the prepolymer is 415-425:

(f) adding 4,4'-methylenebis(3-chloro-2,6-diethylaniline) at an equivalent ratio of 0.95 to 1.02 NH_2 /1.0 NCO; and

(g) curing the polyurethane at 240-275°F.

46. The method of claim 45, wherein, in step (a), said 4,4'-methylenebis(cyclohexyl isocyanate) is mixed with the OH-containing intermediate in an equivalent ratio of 0.96 to 1.0 NH_2 /1.0 NCO.

47. The method of claim 45, wherein the temperature to which the mixture is heated in step (b) is 260-275°F.

48. The method of claim 45, further comprising the step of casting the polyurethane prior to curing the polyurethane.

49. The method of claim 45, wherein the 4,4'-methylenebis(cyclohexyl isocyanate) comprises at least 50% of the trans,trans isomer, and no more than about 20% of the cis,cis isomer.

50. The method of claim 45, further comprising the step of adding an activated polybutene with epoxide functionality at one end to the prepolymer after step (e).

51. The method of claim 50, wherein the activated polybutene is Actipol E6.

52. The method of claim 51, wherein about 2 to 2.5% by weight Actipol E6 is added to the prepolymer.

53. The method of claim 45, further comprising the step of adding a UV-stabilizer to the prepolymer in an amount of about 1.5-2.0% by weight of the prepolymer.

54. The method of claim 53, wherein the UV-stabilizer is selected from the group consisting of Cyabsorb and Tinuvin.

55. The method of claim 45, further comprising the step of adding an anti-oxidant to the prepolymer.

56. The method of claim 55, wherein the anti-oxidant is Irganox.

57. The method of claim 45, further comprising adding a quantity of triol sufficient to produce 1% cross linking based upon equivalents of reactants.

58. The method of claim 57, wherein the triol is selected from the group consisting of trimethylol ethane, trimethylol propane, and mixtures thereof.

59. The method of claim 44, wherein said 4,4'-methylenebis(cyclohexyl isocyanate) is mixed with said OH-containing intermediate in an equivalent ratio of 3 to 3.5 NCO/1.0 OH.

60. The method of claim 44, wherein said OH-containing intermediate has a weight average molecular weight of between about 600 and about 900.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/01425

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08G 18/48

US CL : 528/61, 63, 64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/61, 63, 64

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,963,681 (KANEKO ET AL.) 15 June 1976, note the abstract and column 5, lines 35-68.	1-60



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 MAY 1996

Date of mailing of the international search report

13 JUN 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JEFFREY MULLIS jd

Telephone No. (703) 308-1235

